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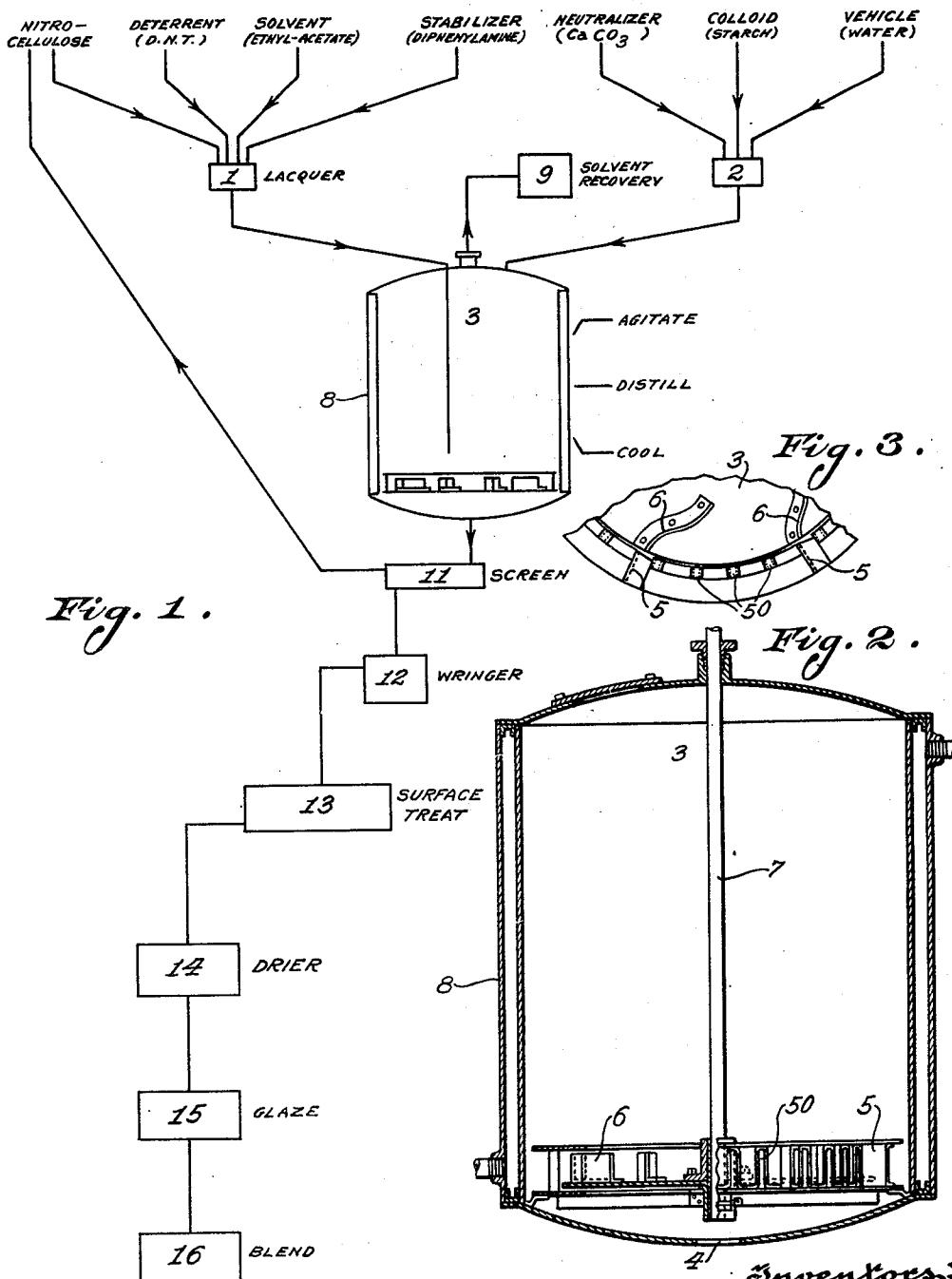
F. OLSEN ET AL

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MANUFACTURE OF SMOKELESS POWDERS

Filed March 12, 1932

3 Sheets-Sheet 1



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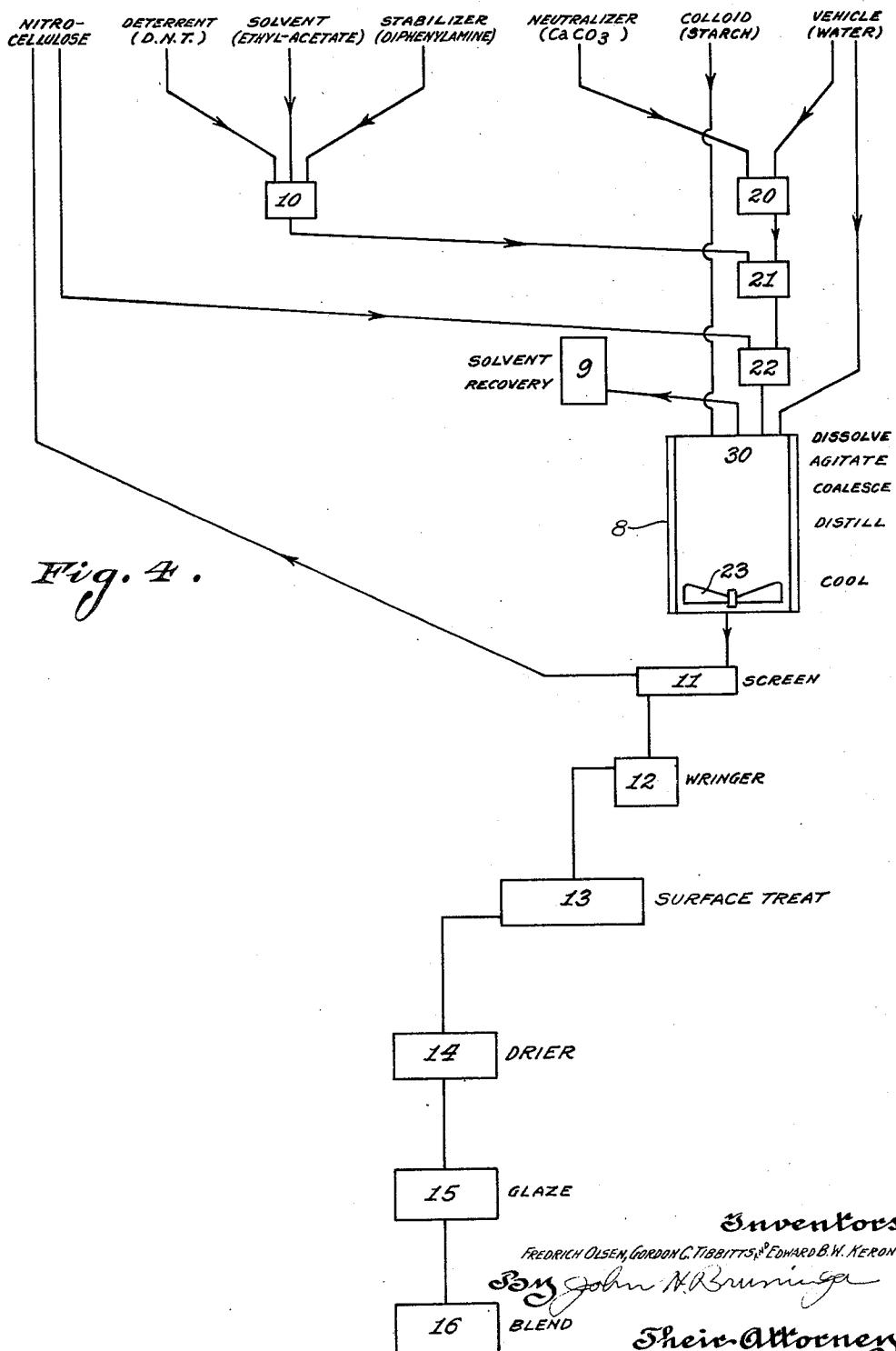
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MANUFACTURE OF SMOKELESS POWDERS

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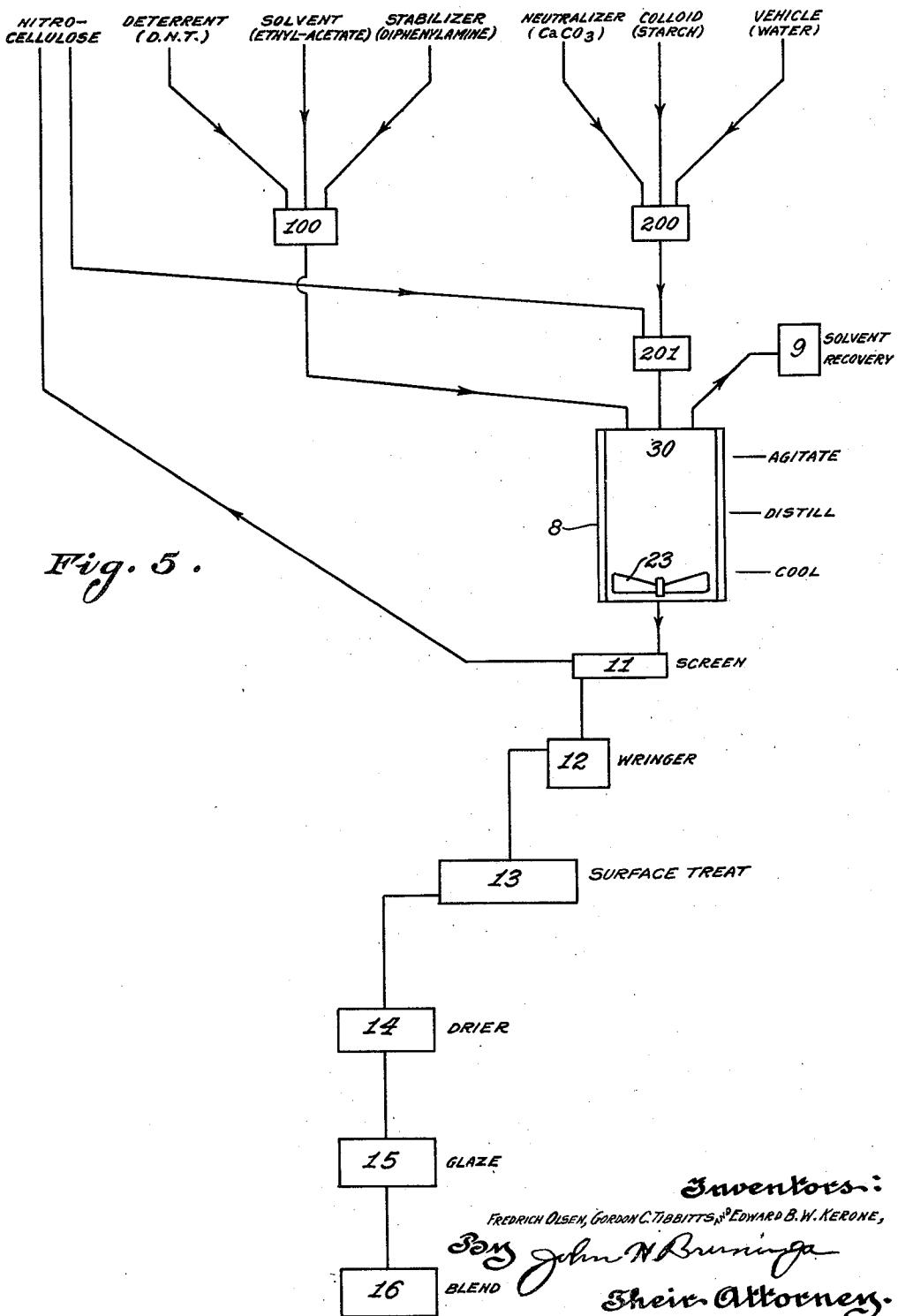
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MANUFACTURE OF SMOKELESS POWDERS

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3 Sheets-Sheet 3



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UNITED STATES PATENT OFFICE

2,027,114

MANUFACTURE OF SMOKELESS POWDERS

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32 Claims. (Cl. 52—22)

This invention relates to the manufacture of explosives and more particularly to the manufacture of smokeless powders, such as those having a base of nitrocellulose.

One of the objects of this invention is to provide a process whereby the operations may be carried out in a manner so as to secure a superior product irrespective (within limits) of the base or material employed, i. e. whether, for instance, freshly prepared or unstable material or deteriorated powder or stock.

Another object is to provide a process whereby, during the course of operations, the product is purified and stabilized; and whereby the incorporation of additional ingredients such as stabilizers and modifying agents, such as deterrents or accelerators may be readily effected.

Another object is to provide a process whereby the production of desirable grains, and more particularly spherical grains is assured.

Another object is to provide a process whereby the procedure may be carried out to secure economy and safety of operation.

Another object is to produce a powder grain of desired form and more particularly spherical in form.

Another object is to provide a powder grain which has incorporated therewith or is surface treated with a modifying agent such as a detergent or an accelerator.

Another object is to provide a powder charge in which the several grains are uniform as to their ignition characteristics or rates of combustion.

Further objects will appear from the detail description in which will be set forth a number of embodiments of this invention; it is to be understood, however, that the embodiments described are illustrative only of various embodiments of which this invention is susceptible. In the following description, as far as possible, an explanation will be given of what is believed to be the action taking place from a theoretical standpoint; it is to be understood, however, that in giving such explanation the theory and explanation is advanced for the purpose of facilitating an understanding from a theoretical standpoint; and it is understood that this invention is not to be limited to any advanced theory or explanation from a theoretical standpoint.

In accordance with this invention the operations are so carried out as to produce grains which are uniform as to shape and preferably spherical, and to an extent the process can be

controlled so as to secure uniformity as to grain size. Generally stated the desired formation of the grains is accomplished by dispersing globules of the base (such as nitrocellulose) in a medium so as to secure the formation of grains of the desired shape and more particularly of spherical form. This is accomplished in accordance with the embodiments of this invention hereafter more fully described, by subjecting the base and a solvent to agitation in a non-solvent medium (such as water) so as to produce globules which are distributed in the medium and these globules are individually consolidated so as to form grains which are spherical. To effect this purpose, there may be employed, a volatile solvent which, after performing its solvent action with the attendant production of globules, is vaporized by heating the medium to the vaporizing point of the solvent, the medium being not only a non-solvent, but also relatively non-volatile at the temperatures employed.

In order to effect efficient distribution, the process is carried on in the presence of what is hereafter descriptively referred to as a protective colloid, and which is believed to perform the function of effecting a quasi-emulsion between the base and solvent and the non-solvent medium, with the base and solvent as the internal phase.

The production of globules, or the production of the quasi-emulsion may be secured in various ways. Thus in accordance with one embodiment of this invention, the base is dissolved in a solvent and the colloidal solution or lacquer is agitated rather violently in a non-solvent vehicle in the presence of the protective colloid to form the globules. In accordance with another embodiment of this invention, the base is agitated with a solvent distributed in the non-solvent vehicle so as to form an emulsion with the medium as the internal phase; upon the addition of the protective colloid the emulsion is broken and under agitation reformed, or as we may say, inverted with the medium as the external phase. In accordance with still another embodiment of this invention, rather large particles of the base are agitated with a solvent distributed in the non-solvent vehicle in the presence of the protective colloid so as to form the globules as the base particles are attacked or softened by the solvent. In all cases, globules are distributed throughout the medium, and these globules are then subjected to treatment to extract the solvent, as by distillation of the solvent secured by heating the medium to near

the vaporizing point of the solvent, or therebeyond.

The distillation is so carried out as to effect a gradual vaporization of the solvent from the several globules; the process is preferably carried out by effecting vaporization at a rate decreasing from the beginning to the end of the vaporization period and at a rate less than the rate of diffusion of the solvent from the interiors to the exteriors of the globules. Such a distillation secures a solid grain as distinguished from one which is hollow and porous.

The process is subject to control so as to pre-determine the size of the grains. This can be accomplished by controlling the extent or violence of the agitation of which the grain size is a function; by controlling the amount of the protective colloid present, of which the grain size is also a function; or by controlling the viscosity of the dissolved or partially dissolved, base of which the grain size is also a function. By controlling these various factors, the grain size may be controlled and predetermined after establishing limits based upon experimental data.

In accordance with this invention, a stabilizer, and even a neutralizer is incorporated with the grain and distributed throughout the grain. This is accomplished in accordance with the various embodiments of the invention by, for instance, incorporating the stabilizer with a solvent and a base to form a lacquer where the base is dissolved prior to its being emulsified with the vehicle or medium; by incorporating the stabilizer in the solvent which is then distributed in the medium or vehicle and thereafter agitated with the base; or by incorporating the stabilizer with a solvent, distributing the same in the medium and subjecting rather large particles of the base to agitation in the medium. In the various embodiments, the stabilizer is not only uniformly distributed throughout the globules formed within the medium and the grains thereafter formed from the globules, but any acidic or deteriorated elements present will be distributed throughout the vehicle or medium. The neutralizer is added to the medium and similarly distributed so as to perform its useful function.

The modifying agent such as a deterrent or accelerator may be incorporated with a grain and distributed throughout the grain in a manner similar to that of incorporating the stabilizer previously referred to, by incorporating the modifying agent with a solvent, as by dissolving the same in the solvent, when it will be carried through the process as previously described in connection with the stabilizer.

After formation of the globules in the medium or vehicle as heretofore described, and after distillation of the solvent from the several globules to form the grains, the medium is permitted to cool to a temperature sufficiently low to permit any modifying agent or stabilizer dissolved in the normally non-solvent medium to separate out at the lower temperature. In the case of the modifying agent, such as a deterrent, it will become deposited on the grains so as to provide a surface treatment in the form of a coating or impregnation.

After cooling of the medium, and when the grains have become consolidated or hardened, they may be subjected to a screening operation. This can be a wet screen process in which the oversizes can be sent back for reworking and the screened grains can be subjected to a wringing operation and thereafter to a drying opera-

tion. The solvent which has been vaporized can be recovered in a suitable solvent recovery apparatus. It will also be noted that not only can the evaporation of the solvent, which is ordinarily inflammable, be accomplished in the presence of a medium such as water which is non-inflammable, but that during the screening, wringing and drying operations there is an absence of inflammable material and the grains are water wet to the last stage of the drying process.

After the grains are dried, they may be subjected to a simple glazing treatment where the grains are not surface treated. These grains may, however, be surface treated prior to drying with a suitable modifying agent, such as a deterrent or an accelerator. They may be then dried and glazed in the usual manner and thereafter blended if desired.

In accordance with an embodiment of this invention, a powder charge can be produced in which the grains have the same rates of burning. This may be accomplished by screening the grains by a series of screening operations, so as to secure a powder charge having grains of substantially the same size, as well as shape. This is possible due to the fact that the grains are spherical as distinguished from angular or oblong. A powder charge comprising portions of normally different rates of burning, as by being composed of even spherical grains of different sizes, may be treated so as to have the same rate of burning. This may be accomplished by treating portions having a higher rate of burning with a deterrent, by treating portions having a lower rate of burning with an accelerator, or by treating two portions respectively with a deterrent and an accelerator, so as to secure a blended charge in which the grains have the same rate of burning.

A number of embodiments of this invention heretofore generally referred to will now be described under the descriptive headings: I. A "Solution or lacquer process"; II. "Distributed solvent process"; III. "Large base particle process"; it will be understood, however, that these headings are simply for classification purposes and are not limitative. These embodiments will be described in connection with the accompanying drawings, in which:

Figure 1 is a diagram illustrating classification I;

Figure 2 is a section showing a detail of what may be called the still, while Figure 3 is a diagram showing the relation of the stator and rotor;

Figure 4 is a diagram illustrating classification II; and

Figure 5 is a diagram illustrating classification III.

In the diagrams, Figures 1, 4 and 5, apparatus parts are shown which may not be essential for the practice of the processes hereinafter described; that is done for the purpose of facilitating the disclosure of the processes and in order to diagrammatically illustrate the steps or operations of the process. As will, however, hereafter appear, a number of operations or steps may be performed in the same container, such as the still with its agitator.

I. Solution or lacquer process

In this embodiment, the base may be nitrocellulose which as to kind and character, as well as composition, may be varied; it may be wholly or partially purified fibrous nitrocellulose in

the form of nitrated flakes, linters, or wood pulp; it may be dense colloided nitrocellulose in the form of existing powder, whether fresh or deteriorated, or of good, poor or indifferent stability; it may be nitrocellulose from other processes such as dust and mud or bulk powder and cannon powder. The nitrocellulose may be of any suitable degree of nitration such as having a nitrogen content of 12.4 to 13.4.

10 The modifying agent employed, and to be incorporated with the powder grain may be any suitable deterrent such as dinitrotoluene, di-
15 amylphthalate or dibutylphthalate. Where DNT is employed its percentage can vary from 10% to 20% relative the weight of the powder.

15 The solvent employed may be any suitable solvent such as ethyl acetate, but any other suitable solvents of nitrocellulose may be employed. Where ethyl acetate is employed in this particular embodiment, it is used in the proportions of five parts to one part of the powder grain.

20 Any suitable stabilizer such as diphenylamine may be employed in the proportion of 1% of the weight of the powder.

25 A suitable neutralizer is calcium carbonate (CaCO_3) in the form of purified prepared chalk which is employed in the proportions of 1% relative the weight of the powder.

30 A suitable protective colloid is starch in the form of corn starch in the proportion of 2% of the weight of the water used as a medium or vehicle. It is prepared by boiling so as to produce a gel. It is preferably of a form which has been prepared by the acid process having a pH 35 value of 5., an acidity value of .085 and an ash content of .12. Other suitable agents for performing the same function may, however, be employed, such as gum arabic, dextrin or bentonite.

40 The medium or vehicle is preferably a non-solvent such as water, having a relatively high boiling point and non-inflammable. It is employed in this embodiment in the proportion of eight times the weight of the powder. Up to the 45 distillation process it can be used at ordinary temperatures, that is from 10° to 20° C.

45 Referring now to Figure 1, the nitrocellulose base, the deterrent, the solvent and the stabilizer may be mixed in a vessel 1 to produce a lacquer. This lacquer may contain from 15% to 25% dissolved nitrocellulose and can have a viscosity of from 300 to 2500 seconds (Falling Ball method) at 25° C.

50 The neutralizer, the colloid and the vehicle may be placed in a vessel 2, it being preferable that the starch be previously formed into a gel by boiling in a small quantity of water, and when added to the eight parts of water there is formed a thin colloidal solution. The vessel 2 may, however, be dispensed with and the calcium carbonate, starch and water may be mixed directly in the vessel 3 hereafter referred to as the still. Into this vessel, the lacquer is later conducted.

55 This still comprises a casing of suitable capacity, closed at the top except for an inlet opening provided with a closure; it is also provided with a discharge opening 4, provided with a closure. It has arranged therein a stator provided with stationary vanes 5 and a rotor provided with blades 6 so as to form what is known as a turbine mixer. The rotor may be driven through a shaft 7 from a suitable source of power. A relation of stator and rotor blades 70 which is particularly suitable is shown in Fig-

ures 3 and 4. While the stator blade 5 is shown as substantially radial, the rotor blade 6 is shaped as shown along a curve with a terminal extending in practically a radial direction. With such a construction the liquid thrown out by centrifugal force by the rotor is violently projected against the stator blades 5 and also against additional blades 50 provided on the stator. The still is also provided with a steam jacket 8 and the top of the still leads to a suitable solvent 10 recovery apparatus 9.

When the contents of the still, including the calcium carbonate, the starch and the water is in violent agitation, the lacquer is conducted into the vortex formed, thereby forming a quasi-emulsion with the lacquer as the internal phase. After the globules have been properly formed, steam is applied to the coil 8 while the agitation is slowed down thereby causing the solvent to vaporize and pass to the recovery apparatus 9. 20 After volatilization of the solvent the contents of the still are allowed to cool to a temperature of about 50° C. The contents of the still are now passed on to a screen 11, from which the oversize is sent back for reworking, while the screened 25 material is sent to a suitable centrifugal wringer 12. It will be understood that the screen 11 may be of a construction so as to size the material into one or more sizes with the oversize, as well as the very fine material, sent back for reworking. 30 From the wringer the powder grains may be surface treated at 13. They may then be sent to a suitable drying apparatus 14, a glazing apparatus 15, and a blending apparatus 16.

Operation

Upon the addition of the lacquer to the vessel 3 containing the water, starch and calcium carbonate under agitation, the lacquer is broken up into globules so as to produce a quasi-emulsion 40 with the lacquer as the internal phase. The formation of the globules and the dispersion of the same throughout the medium is facilitated by the fact that the liquid is projected by the rotor blades against the stator blades.

45 In the formation of the globules from the lacquer, various emulsion phenomena are encountered. While the system, nitrocellulose-solvent-water, tends toward a condition of emulsion corresponding to water-lacquer emulsion with the lacquer as the external phase, this tendency is overcome by the presence of the starch, particularly in the presence of a neutralizing agent such as calcium carbonate, tending to produce an alkaline material. While the action cannot be 50 determined with certainty, it is believed to be connected with surface tension, differential viscosity and adsorption. By Gibbs' Theorem, if a substance lowers the surface tension of water when dissolved in it, that substance will concentrate at interfaces, producing what is termed adsorption. If a substance produces a viscous solution with water, then the water solution will be most viscous near a surface. If a condition has been produced where the emulsion will be 55 one in which the lacquer is the internal phase, as globules or droplets of lacquer are detached by the agitator the colloid becomes adsorbed around each droplet, producing a protected globule. The most viscous layer will be adjacent to the droplet and there will exist a gradient of diminishing viscosity from the surface of the droplet to the main body of the water phase.

60 The way in which the adsorbed film protects two globules from coalescing is believed to be 75

somewhat as follows:—When the medium containing the globules is placed in motion, movement will take place along the plane of least viscosity, which is the plane between the two globules; even if two globules are moving directly toward each other, they will move around each other without touching or coalescing, since movement always takes place along planes of least viscosity. After formation and protection of the globules, the system has a strong tendency towards a condition of minimum surface energy. If it were possible, coalescence would take place to satisfy the condition. Because of this tendency, the globules of lacquer assume the shape which offers least interface, namely spherical.

The size of the globules and of the grains thereafter formed depends upon a number of factors, namely, the grain size decreases with increase of rotor speed, decreases with increase of percentage of the colloid and decreases (within limits) with decrease of inherent viscosity of the nitrocellulose, that is viscosity of a given weight of nitrocellulose in a given quantity of a standard solvent. The grain size also seems to increase (within limits) with decrease of percentage of the solvent.

The distillation procedure operates to remove the solvent; in this procedure, however, care must be taken not to remove the solvent at too high a rate, for otherwise hollow and porous grains having the appearance of popcorn and a corresponding low density will result. If, however, the solvent is evaporated at a slow rate and at a temperature below the boiling point of the solvent, extremely dense spheres will result. The time required for this is however, protracted and may involve a production problem. Advantage can, therefore, be taken of a number of factors including the lower boiling point of a solvent in water emulsion.

Experience has shown that in removing solvent from a lacquer globule, the rate at which solvent can diffuse through the lacquer depends upon viscosity and, therefore, upon the amount of solvent present in the grain. The rate of diffusion must exceed the rate of removal of the solvent or a hard case or skin is formed around the globule which does not thereafter soften and the grain formed shows that shrinkage of the nitrocellulose upon the inner face of this case has taken place so as to form a hollow shell. One of the problems is, therefore, the removal of the solvent at a proper rate to produce solid as distinguished from hollow and porous shells. In accordance with this invention the removal of the solvent is so controlled that the solvent is removed at a rapid rate at the beginning and thereafter at a decreased rate until the grain becomes case hardened. After case hardening, the solvent can be removed at a reasonable rate without appreciably affecting the density. As a practical illustration, during the case-hardening period, distillation is started at a temperature of 68° C., and the heat is so maintained that over a period of 65 minutes, the temperature will rise to 72° C. This is really a distillation at a decreased rate, for at a uniform rate the temperature at the end of the case-hardening period would be much higher than 72° C.; accordingly, although the temperature may, therefore, rise, the distillation is really at a decreased rate. After such case-hardening period, the temperature can be raised to 95° C. until the solvent has been expelled.

During the distillation period, the contents of the still are kept in agitation, although the agitation need not be as violent as during the forma-

tion of the globules. At the end of the distillation period the contents of the still are allowed to cool to about 50° C. as previously described and at this temperature such of the modifying agent (such as DNT) as is in the water is deposited on the grains so as to form in effect a coating.

II. Distributed solvent process

The materials employed are generally the same as in Process I heretofore described, except that the relation of the solvent to nitrocellulose can be decreased to a point 4 to 1 and even to a point 2.5 to 1. The process is generally as follows:

Referring to Figure 4, the deterrent, solvent and stabilizer can be mixed in a vessel 10, while the calcium carbonate and the water can be mixed in a vessel 20 and the contents of both can be then mixed in a vessel 21. The contents of vessel 21 can then be passed to a vessel 22 into which the nitrocellulose is discharged, and the contents of 22 can finally be discharged into a vessel 30 which may again be a still provided with an agitator 23 and a steam coil 8. The agitator may, however, be of the simple paddle form and need not be of the turbine mixer form. It will be understood that the nitrocellulose, deterrent, solvent, stabilizer, calcium carbonate, and the water may be initially mixed in the vessel 30. The vessel 30 may be otherwise of the form shown in Figure 2, may have an outlet discharge on to the screen 11, and a vapor outlet to the solvent recovery apparatus 9.

Assuming the materials (other than the starch) to be mixed in the vessel 30, it being here noted that the amount of water is 1½ times the weight of the nitrocellulose, agitation is proceeded with until not only the nitrocellulose, deterrent and stabilizer have become dissolved, but until a portion of the water has been emulsified with the lacquer. This results in an emulsion with water as the internal phase and the resultant lacquer as the external phase, although the lacquer phase may not be completely continuous. Agitation can now be stopped to allow the emulsion to settle out from the unemulsified water and consolidate in one large piece of emulsion instead of several pieces. The temperature in this case is preferably maintained at about 50° C.

The starch prepared as previously described in connection with Process I so as to form a gel, is now added to the still and 6 parts of water compared to the weight of the nitrocellulose added; or the starch gel is previously mixed with the 6 parts of water and added to the vessel 30; this is preferably done while the contents of the vessel are in agitation. Upon the addition of the colloid, the emulsion previously formed is broken and inverted so as to produce a quasi-emulsion with the water as the external phase and with the lacquer as the internal phase so as to again distribute globules of the base-solvent, etc., throughout the medium or vehicle. Distillation, cooling, screening, etc., can then be proceeded with as previously described in connection with Process I.

This process has an advantage over Process I in that it is not necessary to preliminarily dissolve the nitrocellulose in the solvent, but the solvent is distributed throughout the vehicle or medium and attacking the nitrocellulose dissolves the same. The proportion of solvent can accordingly be lowered to 4 to 1 and even to 2½ to 1 as distinguished from 5 to 1. The production of spherical grains is again secured as in Process I and again nitrocellulose in any suitable form as

in Process I can be employed, the temperature previous to distillation is in this process raised to 50° C. so as to effect more efficient and rapid solution of the nitrocellulose, the solution period 5 being 2-4 hours in case cannon powder is used as a base.

III. Large base particle process

The materials for this process are the same 10 as in Processes I and II previously described, except that it is only practical to employ large grains, particularly of dense colloid nitrocellulose, an example of which is deteriorated cannon powder. It is not practical to employ fine grained 15 powder. The ratio of solvent to powder can be 4 to 1 and even 3 to 1.

The deterrent, solvent and the stabilizer can 20 be mixed in a vessel 100 (Fig. 5) calcium carbonate, starch and water can be mixed in a vessel 200 with about 7½ parts of water, compared with the weight of the nitrocellulose, the starch being 25 prepared as previously described in connection with Process I. The nitrocellulose and the contents of vessel 200 can then be mixed in a vessel 201 and the contents of the latter discharged 30 into the vessel 30, which may be of the same construction as described in connection with Process II and which may have a vapor outlet to the solvent recovery apparatus 9, and may lead to the material outlet on the screen 11 as previously 35 described. It is understood, however, that the nitrocellulose, calcium carbonate, starch and water may be mixed in vessel 30. While the mass is in agitation, the contents of vessel 100 may be 40 added to the vessel 30 or all of the materials may be added to vessel 30 and mixed therein.

In the vessel 30, agitation is carried on for a period of about two hours at about 20° C., which 45 is the normal temperature of the water as obtained from the supply. This results in the formation of globules distributed throughout the medium or vehicle. At the completion of this period distillation is proceeded with as described in Processes I and II, the contents of the vessel 50 allowed to cool and the material screened, wrung, dried, etc., as previously described.

While the formation of globules may be accomplished by the solvent action of the solvent distributed throughout the medium and attacking 55 the nitrocellulose, the action is believed to be somewhat as follows:—The water and solvent form an emulsion comprising droplets of solvent in the water. These droplets attack the nitrocellulose grains promoting softening, as well as swelling of the same. The violence of the agitation causes portions of the gelatinized portions of the nitrocellulose to be removed from the grains so as to assume globular form in the water medium. The violence of agitation, the ratio of 60 solvent to nitrocellulose, and the ratio of water to nitrocellulose again influences the size of the particles formed, so that the production of uniform spherical grains of predetermined granulation can be produced. Variations in gravimetric 65 density and in granulation can be affected by appropriate changes in the above mentioned factors.

The starch plays an important part in this process, for when it is employed, as previously 70 described, spherical grains are produced, except for small angular grains which seem to be the residue of the original grains of nitrocellulose and which can be discarded by screening. If no starch is used, then flaky grains are produced.

75 The process has the advantage that the period

required for the formation of the globules is two hours as compared to fourteen hours required in Process I when ordinary cannon powder is used.

As previously stated, such colloids as gum arabic, dextrin or bentonite may be used. Where 5 gum arabic is used it may be employed in the proportion of 1% relative the weight of the water.

Incorporation of stabilizer and neutralizer

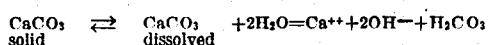
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Nitrocellulose in general and cannon powder in particular decomposes in spots. These spots are centers of high acid content and contain no unnnitrated diphenylamine to absorb the acid which is being liberated. Furthermore, while 15 diphenylamine is a neutral amine, its nitration products nitrosodiphenylamine, nitrodiphenylamine, dinitrodiphenylamine and trinitrodiphenylamine are acidic, and in large quantities such as are present in one of these spots may be antagonistic toward nitrocellulose. Various decomposition products such as ether peroxide formed by oxidation of the residual ether, ethyl nitrate 20 formed by alcoholysis of the nitrocellulose by the residual alcohol, and the possible presence of 25 cellulose nitrite would help explain the unstable character of some cannon powders.

In accordance with this invention, as described 30 in the various embodiments, the nitrocellulose, even if deteriorated is purified and stabilized. That is particularly true where the nitrocellulose is actually dissolved as in the Processes I and II and even in Process III where the nitrocellulose is partially dissolved and at least gelatinized. By this action the nitric acid present in the spots 35 is liberated and spread uniformly throughout the solution. This is important since a small amount of acid uniformly distributed through nitrocellulose might not be harmful, whereas this same quantity of acid when locally concentrated would 40 be injurious. The acidic nitrated diphenylamines are also brought into homogenous solution, and diphenylamine which could not be reached by the nitric acid is brought into intimate contact therewith. More diphenylamine is 45 usually added to the solution as a further safeguard.

When the dissolved, or partially dissolved or 50 gelatinized nitrocellulose is mixed intimately with water containing calcium carbonate, acid diffuses out into the water and is neutralized. This alkaline medium also has a hydrolyzing action 55 upon any unstable esters which may be present and the solvent action of the water frees the solution of ether peroxide if such is present.

A mild alkaline material like calcium carbonate 60 was chosen for the following reasons:—When calcium carbonate is suspended in water some of it dissolves setting up the following equilibrium:



The concentration of OH ion is large enough to 65 neutralize acids (which shifts the equilibrium to the right) but not large enough to injure the nitrocellulose. As soon as some of the OH ions are neutralized, more undissolved calcium carbonate dissolves and hydrolyzes.

The calcium carbonate is also believed to perform a useful function to render effective or increase the efficiency of the starch in performing 70 its useful function in the processes so as to secure the formation of globules and consequently spherical grains.

In Process II an additional means of purifica- 75

tion is afforded by emulsifying some of the water containing calcium carbonate within the lacquer solution, the nitrocellulose acting in this instance as the emulsifying agent. This emulsion is later 5 broken by the colloid present in the remaining part of the water and the phases reversed to form globules of lacquer in water.

Incorporation of modifier

10 In accordance with this invention, as illustrated in the various embodiments, the modifying agent such as a deterrent is uniformly distributed throughout the grain. This is efficiently accomplished in the embodiment described by 15 dissolving the deterrent in ethyl acetate which, in addition to being a solvent for nitrocellulose is also a solvent for DNT. In Process I this modifier is distributed throughout the lacquer, and this is also true in Process II where the modifying 20 agent is again distributed throughout the globules. This is even true of Process III where the modifying agent again enters the nitrocellulose with the solvent.

Upon vaporization of the solvent, the modifying 25 agent is left in the grain, except such parts as may dissolve in the water at the distillation temperature. Upon cooling of the water, however, it separates from the water and coats or impregnates the grains.

30 *Grain formation*

As previously described, the powder produced is not only substantially spherical in shape but uniformly dense. It, therefore, has advantages 35 not only from a ballistic standpoint but also from a loading standpoint. Spherical grains of the same size and composition burn at the same rates. Accordingly by screening grains closely the same size can be secured. That is impossible with angular or oblong grains which, on account of their 40 varying shapes have different volumes, even though all may pass through the same screen opening. In accordance with this invention there is, therefore, produced, a powder charge in which 45 the various grains of the charge have the same rate of burning and even the same igniting characteristics.

From a loading standpoint the spherical grain shape and the ability to readily screen to the 50 same size are advantageous in that it is possible to secure, even by volumetric loading, a powder charge whose ballistic characteristics can be more accurately controlled; for packing in a cartridge is not a matter of chance as with flaky or 55 angular grains where the weight per volume depends upon the arrangement of the grains in the charge. Spherical grains also flow easily.

The powder presents a wide range of possibilities since it can be prepared from a mixture of 60 nitrocellulose having different potentials and different degrees of nitration; furthermore, by the incorporation of modifiers such as deterrents and accelerators, the ballistic characteristics may be varied particularly since they can be uniformly 65 incorporated. These also serve to improve the gel structure and resistance to moisture.

The uniformity of grain size, shape and composition of the powder embodying this invention 70 also has the following advantages over grains prepared by cutting slices from an extruded cord, because it is impossible to obtain the degree of uniformity with the latter type that is attained by the powder embodying this invention; for the 75 mechanical aberrations of the cutting equipment will be such that the slices are wedge shaped,

thereby producing an unevenness of web thickness that affects the uniformity of burning which is achieved by closely sized spherical grains.

Surface treating and blending

The powder grains embodying this invention can be surface treated with any suitable modifying agent such as a deterrent or an accelerator. An example of a deterrent is DNT, while 10 an example of an accelerator is nitroglycerine. The surface treatment may be performed in any suitable manner so as to secure the desired ballistic results. In applying a deterrent such as DNT it may be applied with any suitable emulsifying agent such as saponin in water, or the 15 emulsion may be diluted and added to an agitating slurry of water and the powder. In the application of an accelerator such as nitroglycerine, it may be added to a water and powder slurry in the form of an alcohol-benzol solution, 20 the alcohol and benzol being evaporated. The surface treated powder grains may be given a water-dry treatment to insure a hard surface and to improve the flowing property of the grains. These grains may then be glazed in the usual 25 way.

Powder of varied grain size may be blended to 30 secure the desired ballistic properties. Grains of different sizes may be treated to secure the same rates of burning; thus grains of larger size may 35 be surface treated with an accelerator such as nitroglycerine; grains of smaller size may be surface treated with a deterrent such as DNT or grains of two sizes may be treated, one with an accelerator and the other with a deterrent so as 40 to secure the same rates of burning. In this way the blended charge, although of different grain sizes will be such that all of the grains of the charge will have the same rates of burning.

Again the ballistic characteristics of the powder 45 may be controlled by suitable surface treatment variation consisting in coating the grains after they have been completely formed with DNT or the like for the purpose of increasing the rate of burning or improving the ease of ignition.

In case coarse grained powder be coated with nitroglycerine and blended with the finer material, either uncoated or coated with DNT, improved hygroscopicity and improved ignitability 50 will be secured through the use of portions of the nitroglycerine coated powder blended with the uncoated or DNT coated finer material.

Close control in granulation made possible by the spherical powder enables the load to be so 55 designed that none of the particles are sufficiently large as to remain unburned. On the other hand, an additional factor of safety is secured by only coating the screened portion which is finer than the average, avoiding thereby the slow- 60 ing of the particles of coarser granulation. This condition can be still further enhanced when the larger particles are nitroglycerine-coated as this tends not only to improve the ignitability of these larger particles, but also to increase their rate 65 of burning.

It will be understood that while in the embodiments described, the explosive or powder base has been nitrocellulose, various other powder and explosive bases may be employed to secure many 70 of the advantages of this invention. It will also be understood that various combinations and sub-combinations may be employed to secure many of the advantages of this invention without reference to other combinations and subcombi- 75

nations; that is contemplated by and within the scope of the appended claims. It will further be understood that various changes may be made in details without departing from the spirit of this invention; it will, therefore, be understood that this invention is not to be limited to the various details described.

Having thus described the invention, what is claimed is:

10 1. In the art of making explosives, the process comprising, agitating nitrocellulose and its solvent with an excess of a non-solvent in the presence of a protective colloid and extracting the solvent.

15 2. In the art of making explosives, the process comprising, dissolving nitrocellulose in a solvent, agitating the solution with an excess of non-solvent vehicle in the presence of a protective colloid and extracting the solvent during agitation.

20 3. In the art of making explosives, the process comprising, dissolving a smokeless powder base in a volatile solvent, agitating the solution with an excess of a non-solvent vehicle in the presence of a protective colloid and heating the vehicle to the vaporizing point of the solvent during agitation.

25 4. In the art of making globular smokeless powder grains, the process comprising, dissolving a smokeless powder base and a deterrent in a solvent, agitating the solution with a vehicle which is substantially a non-solvent for the base and solvent to an extent sufficient to form globules and extracting the solvent from the globules.

30 5. In the art of making globular smokeless powder grains, the process comprising, dissolving a smokeless powder base and a stabilizer in a solvent, agitating the solution with a vehicle which is non-solvent for the base and solvent to an extent sufficient to form globules and extracting the solvent from the globules.

35 6. In the art of making explosives, the process comprising, agitating nitrocellulose with a solvent distributed in a non-solvent vehicle and adding a protective colloid.

40 7. In the art of making explosives, the process comprising, agitating nitrocellulose with a solvent distributed in a non-solvent vehicle to effect solution of the nitrocellulose in the distributed solvent, adding a protective colloid and extracting the solvent.

45 8. In the art of making explosives, the process comprising, agitating nitrocellulose with a volatile solvent distributed in a non-solvent vehicle to effect solution of the nitrocellulose in the distributed solvent, adding a protective colloid and heating the vehicle to the vaporizing point of the solvent.

50 9. In the art of making explosives, the process comprising, agitating a smokeless powder base with a deterrent and a solvent distributed in an excess of a vehicle which is substantially immiscible with the solvent to form globules of the base and the deterrent dissolved in the solvent in the vehicle and heating the mixture to vaporize the solvent from the globules.

55 10. In the art of making explosives, the process comprising, agitating a smokeless powder base with a stabilizer and a solvent distributed in a vehicle which is substantially immiscible with the solvent to form globules of the base, the stabilizer and the solvent in the vehicle and heating the mixture to vaporize the solvent from the globules.

60 11. In the art of making explosives, the process comprising, agitating nitrocellulose with a sol-

vent distributed in an excess of a non-solvent vehicle in the presence of a protective colloid.

12. In the art of making explosives, the process comprising, agitating nitrocellulose with a volatile solvent distributed in an excess of a non-solvent vehicle in the presence of a protective colloid and heating the vehicle to the vaporizing point of the solvent.

13. In the art of making explosives, the process comprising, agitating nitrocellulose with a stabilizer and a solvent distributed in a non-solvent vehicle in the presence of a protective colloid.

15 14. In the art of making explosives, the process comprising, forming and dispersing globules of a smokeless powder base and a volatile solvent in a non-solvent medium and heating the medium to effect vaporization of the solvent from the globules at a rate decreasing from the beginning to the end of the vaporization.

20 15. In the art of making explosives, the process comprising, forming and dispersing globules of a smokeless powder base and a volatile solvent in a non-solvent medium and heating the medium to effect vaporization of the solvent from the globules at a rate less than the rate of diffusion of 25 the solvent from the interiors to the exteriors of the globules.

25 16. In the art of making globular smokeless powder grains, the process comprising, dissolving a smokeless powder base in a solvent, distributing 30 a stabilizer throughout the dissolved base, forming the dissolved base into globules and extracting the solvent.

35 17. In the art of making globular smokeless powder grains, the process comprising, dissolving a smokeless powder base in a substantially non-water-soluble solvent, distributing a deterrent throughout the dissolved base, forming the dissolved base into globules and extracting the solvent.

40 18. In the art of making explosives, the process comprising, introducing nitrocellulose and a solvent into a non-solvent vehicle in the presence of a protective colloid with attendant agitation to form grains and controlling the grain size by the amount of colloid present.

45 19. In the art of making explosives, the process comprising, forming and dispersing globules of nitrocellulose solution in an excess of non-solvent medium, and solidifying the globules while 50 in dispersion.

55 20. In the art of making explosives, the process comprising, agitating nitrocellulose particles of substantial size in a non-solvent vehicle, bombarding the particles with globules of solvent, and 55 removing the solvent.

60 21. In the art of making explosives, the process comprising, agitating a smokeless powder base in a non-solvent vehicle with solvent which is substantially immiscible with the vehicle, sufficient 60 to form globules of dissolved base, and thereafter removing the solvent from the globules.

65 22. In the art of making explosives, the process comprising, agitating a smokeless powder base with a solvent distributed in a non-solvent vehicle to effect an emulsion, and adding a protective colloid to the emulsion.

70 23. In the art of making explosives, the process comprising, agitating a smokeless powder base with a solvent distributed in a non-solvent vehicle to effect an emulsion, adding a protective colloid to the emulsion, and heating the vehicle to the vaporizing point of the solvent.

75 24. In the art of making propellant powder grains, the process comprising, forming a solu-

tion of nitrocellulose in a solvent which is substantially immiscible with water and boils below the boiling point of water, the solvent employed being 2.5-6 times the weight of nitrocellulose, 5 agitating the solution in 6 to 8 times its weight of water to form globules of nitrocellulose lacquer dispersed in the water, and heating the mixture to the vaporizing point of the solvent while the globules are maintained in dispersion.

10 25. In the art of making globular smokeless powder grains, the process comprising, dissolving a smokeless powder base in a volatile solvent, agitating the solution with a non-solvent vehicle to form globules and distribute the same throughout the vehicle, and heating the vehicle to the vaporizing point of the solvent while the distribution of the globules is maintained.

15 26. In the art of making explosives, the process comprising, agitating nitrocellulose with a volatile solvent distributed in a non-solvent vehicle at normal atmospheric temperature to form globules in the vehicle, and thereafter heating the vehicle to the vaporizing point of the solvent while the distribution of the globules is maintained.

20 27. In the art of making explosives, the process

comprising, dispersing globules of a smokeless powder base and a volatile solvent in an excess of a non-solvent medium at substantially normal atmospheric temperature, and heating the medium to effect gradual vaporization of the solvent from the globules while dispersed. 5

28. In the art of making explosives, the process comprising, agitating nitrocellulose with a deterrent and a solvent distributed in an excess of a non-solvent vehicle in the presence of a protective colloid. 10

29. A propellant powder grain comprising, a solidified droplet of a gelatinized smokeless powder base, surface treated with a modifying agent. 15

30. A propellant powder grain which is a solidified droplet of gelatinized smokeless powder base. 15

31. A propellant powder grain comprising a solidified droplet of a gelatinized smokeless powder base surface treated with nitroglycerine. 15

32. A propellant powder grain comprising a solidified droplet of a gelatinized smokeless powder base surface treated with a deterrent. 20

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